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Projected Hartree Product Wavefunctions. IV. Radial Correlation in Some Three- and Four-Electron Atoms*

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The energies of some three- and four-electron atoms including radial correlation have been determined by a spin-free version of the projected Hartree–Fock method. The wavefunction possesses the maximum flexibility allowable under the general restrictions of the method, and it is shown that this flexibility is necessary to adequately account for the differences between intra- and intershell correlation. Some comments on the AMO method are included.

I. INTRODUCTION

In articles I[1] and II[2] of this series a method is described for using the theory of symmetric groups in doing a projected Hartree–Fock[3] (optimization after projection) treatment of an atomic or molecular system. In general, the projection involves both spatial and identity symmetries, and such a treatment was given for H_2 in III.[4] However, we may study the effect on the correlation energy of various factors in the treatment without the added complication of spatial symmetry projections, by looking at radial correlation in some simple atoms.

The present method, a different-orbitals-for-different-spins (DODS) calculation, is an extension of the independent particle model, in which the wavefunction is given as a projected Hartree product (PHP) made up of n single-particle spatial orbitals for n electrons, that is

$$\phi = \prod_{i=1}^{n} u_i(i). \tag{1}$$

The energy for a pure spin state of S may be obtained from a primitive idempotent of the group algebra of S_n associated with the Young tableau $[2^{(n/2)-S}, 1^{2S}] = [\mu]$, $e^{(\mu)}$. Thus, we have,

$$E = \langle \phi \mid He^{(\mu)} \mid \phi \rangle / \langle \phi \mid e^{(\mu)} \mid \phi \rangle, \tag{2}$$

for a spin-free Hamiltonian, H. As was pointed out in II, where the f_μ standard tableaux of shape $[\mu]$ and if $\pi_1(=I), \pi_2, \cdots, \pi_f$, are the permutations giving the ith tableau from the first, we may usually improve the energy expression by replacing Eq. (2) by

$$E = \langle \psi \mid He^{(\mu)} \mid \psi \rangle / \langle \psi \mid e^{(\mu)} \mid \psi \rangle, \tag{3}$$

where

$$\psi = \sum_{i=1}^{f} \gamma_i \pi_i \phi. \tag{4}$$

In our procedure the energy E is minimized with respect to the γ_i in addition to the orbitals, u_i. As we shall see, the values of the γ_i's can have a profound effect on the way the PHP method produces correlation.

Matsen *et al.*[5] have used a formulation of the energy expression very similar to Eq. (4). Goddard[6] and Kaldor, Schaefer, and Harris[7] have given equivalent treatments of some simple atoms which is equivalent to the present one if a certain fixed set of γ_i's is used.

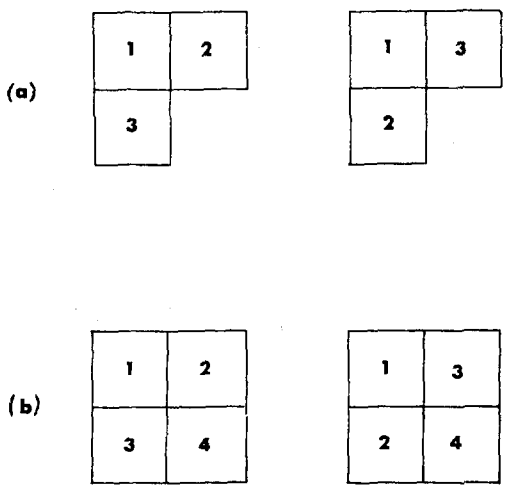

FIG. 1. Standard tableaux for (a) three-electron systems and (b) four-electron systems.

Ritter, Pauncz, and Appel[8] have given a treatment of Li equivalent to the present calculation with a fixed set of γ_i's different from Goddard's choice. More recently, Lunell[9] has given a calculation of Li in which the γ_i's are optimized, but the orbitals are but partially optimized.

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[1] G. A. Gallup, J. Chem. Phys. **48**, 1752 (1968).

[2] G. A. Gallup, J. Chem. Phys. **50**, 1206 (1969).

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[5] F. A. Matsen, Advan. Quantum Chem. **1**, 59 (1964); J. Phys. Chem. **68**, 3282 (1964); **70**, 1568 (1966); F. A. Matsen, A. A. Cantu, and R. D. Poshusta, *ibid.* **70**, 1558 (1966).

[6] W. A. Goddard, Phys. Rev. **157**, 73, 81, 93 (1967); J. Chem. Phys. **48**, 1008 (1968).

[7] U. Kaldor, H. F. Schaefer, and F. E. Harris, Intern. J. Quantum Chem. **2S**, 13 (1968).

[8] Z. W. Ritter, R. Pauncz, and K. Appel, J. Chem. Phys. **35**, 571 (1961).

[9] S. Lunell, Phys. Rev. **173**, 85 (1968).

These previous calculations on the simple atoms include the possibility of radial correlation only, and as was mentioned above, we shall make a similar restriction in the present treatment.

II. THREE-ELECTRON ATOMS

As was pointed out in II, we seem to have fewer computational difficulties by using θNPN for $e^{(\omega)}$ than by using $\theta' PNP$ and this choice is taken. There are three orbitals in these atoms, which shall be designated a, b, and c. Thus

$$\phi = a(1)b(2)c(3), \tag{5}$$

and each of these orbitals is represented as a linear combination of STO's. Table I gives the principle quantum number and the fully optimized ζ's for the three-electron atoms considered here. Figure 1(a) shows the two standard tableaux for doublet states of three electrons, from which it is seen that $\pi_1 = I$, $\pi_2 = (23)$, and hence

$$e^{(2,1)}\psi = e^{(2,1)}[\gamma_1 a(1)b(2)c(3) + \gamma_2 a(1)c(2)b(3)]. \tag{6}$$

The choices among the several alternatives we have made in setting up Eq. (6), now forces a to be the $2s$-like orbital and b and c to be the two $1s$-like orbitals. Table II gives the energies, orbital coefficients, and the γ_i's for each of the nuclear charges considered. Roothaan, Sachs, and Weiss[10] have given restricted SCF energies for these systems, and the correlation energies are also shown. These results are most easily compared with Goddard's,[6] and it is seen that his restriction ($\gamma_2 = 0$) prevents obtaining any considerable correlation energy. The calculation by Pauncz *et al.*[8] corresponds to the restriction $\gamma_1 = \gamma_2$, and as can be seen this is very close to the optimal situation.

We have used the iterative solution outlined in I with one exception: The starting orbitals for b and c are obtained from a calculation of the corresponding two-electron atom first. Then, a third electron is added, and all three orbitals are optimized. If arbitrary starting orbitals are used for a concerted three-electron optimization, it is possible to reach a *cul de sac* (but apparently not a local minimum) in the iteration from which this type of first-order iterative procedure cannot

TABLE I. ζ for three-electron atoms.

	Li	Be^+	B^{++}	C^{+++}
$1s$	4.56	6.01	7.61	9.10
$2s$	4.13	5.50	7.01	8.10
$1s$	2.69	3.52	4.46	5.40
$2s$	2.12	2.81	3.61	4.30
$1s$	0.795	1.01	1.28	1.60
$2s$	0.617	0.811	1.11	1.30
$2s$	0.279	0.211	0.251	0.310
$3s$	0.099	0.111	0.136	0.160

[10] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

TABLE II. Orbital coefficients, γ's, and energies for three-electron atoms.

Li			Be^+			B^{++}			C^{+++}		
a	b	c	a	b	c	a	b	c	a	b	c
−0.05545[a]	0.78281	−0.65198	−0.13285	0.75759	−0.55926	−0.10003	0.28369	−1.00376	−0.05463	0.94743	−0.72222
−0.04424	0.53927	−0.58335	−0.10199	0.50224	−0.49018	−0.07455	0.17761	−0.84043	−0.04682	0.71326	−0.64539
0.11608	−0.49787	2.00682	0.20950	−0.43346	1.89204	0.12015	−0.08501	3.73156	0.00126	−0.86231	2.25756
−0.13538	0.25724	−0.10901	−0.42185	0.24885	−0.19685	−0.42365	0.08168	−0.35714	−0.40117	0.35702	−0.32577
0.16567	−0.09434	0.06704	0.81596	−0.08970	0.08002	0.97194	−0.02843	0.13552	1.03681	−0.14690	0.13563
0.52572	0.03353	−0.02406	0.10340	0.03038	−0.02697	−0.03572	0.01019	−0.04835	−0.07530	0.04866	−0.04462
−0.02069	−0.00657	0.00477	−0.00956	−0.00338	0.00302	−0.00187	−0.00082	0.00386	0.00176	−0.00472	0.00431
0.00241	0.00096	−0.00070	0.00341	0.00125	−0.00112	0.00077	0.00030	−0.00142	−0.00058	0.00179	−0.00163
	$\gamma_1 = 1.00664$			$\gamma_1 = 1.00980$			$\gamma_1 = 1.00967$			$\gamma_1 = 1.00983$	
	$\gamma_2 = 0.99323$			$\gamma_2 = 0.98996$			$\gamma_2 = 0.98995$			$\gamma_2 = 0.98980$	
	$E = -7.44733$ a.u.			$E = -14.2908$			$E = -23.3894$			$E = -34.7397$	
	$E_{corr} = 0.0146$[b]			$E_{corr} = 0.013$			$E_{corr} = 0.013$			$E_{corr} = 0.013$	

[a] These are ordered to correspond to Table I.

[b] E(RSCF) − E(PHP).

TABLE III. ζ for four-electron atoms.

	Be	B^+	C^{++}
1s	6.00	7.60	9.00
2s	5.60	7.00	8.00
1s	3.53	4.44	5.30
2s	2.81	3.60	4.20
1s	1.00	1.22	1.50
2s	0.810	1.20	1.20
2s	0.210	0.350	0.400
3s	0.110	0.110	0.150

depart in a practical length of time. The above type of "building up" procedure prevents this unhappy occurance, and is very similar to that used by Pauncz *et al.*[8] and Lunell.[9] For a given set of ζ's the above procedure for three-electron atoms requires approximately 90 sec on an IBM 360/65 computer. It may be pointed out that a full CI calculation from this basis contains 168 functions.

III. FOUR-ELECTRON ATOMS

Figure 1(b) gives the two standard tableaux for four electrons in a singlet state. We designate the four orbitals a, b, c, d, and thus

$$\phi = a(1)b(2)c(3)d(4), \tag{7}$$

$$\psi = \gamma_1 a(1)b(2)c(3)d(4) + \gamma_2 a(1)c(2)b(3)d(4). \tag{8}$$

Tables III and IV give the results for this case. It is observed that b and c are the 1s-like orbitals and a and d the 2s-like orbitals. The time here is of the order of 270 sec for one ζ set, and the corresponding full CI contains 112 functions.

IV. DISCUSSION

If the results given here are compared with various previous calculations, it is seen that there are a number of interesting points to be investigated. The situations are somewhat different for the cases of three and four electrons, and we take up the smaller case first.

It should be pointed ont that the primitive idempotent $e^{(2,1)}$ contains a factor $[I-(12)]$, and in any term of our wavefunction, the orbitals occupied by electrons 1 and 2 may be orthogonalized to give a term with at most a different numerical factor.

In order to make the analysis it is convenient to introduce two new orbitals,

$$x = \tfrac{1}{2}(a+b), \tag{9}$$

$$y = \tfrac{1}{2}(a-b), \tag{10}$$

where

$$\langle x \mid y \rangle = 0, \tag{11}$$

if a and b are normalized. Using Eq. (6) it is seen that

$$\Phi \equiv e^{(2,1)}\psi = e^{(2,1)}\{(\gamma_1+\gamma_2)[a(1)x(2)x(3) - a(1)y(2)y(3)] + (\gamma_1-\gamma_2)[a(1)x(2)y(3) - a(1)y(2)x(3)]\}. \tag{12}$$

TABLE IV. Orbital coefficients, γ's, and energies for four-electron systems.

Be				B^+				C^{++}			
a	b	c	d	a	b	c	d	a	b	c	d
−0.07998[a]	0.75530	−0.54684	0.02656	−0.01262	0.67157	−0.45875	−0.09162	0.28050	0.82366	−0.60916	−0.45697
−0.05383	0.49710	−0.47491	0.01126	−0.00723	0.42623	−0.38623	−0.07647	0.22463	0.58766	−0.54477	−0.38234
0.05174	−0.43339	1.86536	0.00818	−0.10909	−0.26358	1.69385	0.24583	−0.69272	−0.63057	2.06626	0.85933
−0.41000	0.25428	−0.19493	0.07666	−0.36548	0.20104	−0.18878	−0.15838	−0.04339	0.21887	−0.27681	−0.75999
0.92981	−0.08112	0.07798	−0.19634	1.15942	−0.05110	0.09080	0.11862	0.89947	0.04581	0.09906	1.12440
0.00957	0.04142	−0.02565	0.86844	−0.23015	0.04974	−0.03312	0.69891	−0.11095	0.03029	−0.03429	0.09598
0.00384	−0.00356	0.00295	−0.01618	0.00651	−0.00288	0.00220	−0.02195	0.00983	−0.00482	0.00471	−0.01657
−0.00134	0.00130	−0.00108	0.00571	−0.00093	0.00042	−0.00033	0.00305	−0.00186	0.00098	−0.00095	0.00322
	$\gamma_1=1.03450$				$\gamma_1=1.03897$				$\gamma_1=1.04422$		
	$\gamma_2=0.96533$				$\gamma_2=0.96082$				$\gamma_2=0.95827$		
	$E=-14.5900$ a.u.				$E=-24.2537$				$E=-36.4244$		
	$E_{corr}=0.017$[b]				$E_{corr}=0.016$				$E_{corr}=0.015$		

[a] These are ordered to correspond to Table III.

[b] E(RSCF) − E(PHP).

TABLE V. Radial correlation energy for three- and four-electron atoms.

Type of calculation	Energy (a.u.)						
	Li	Be^+	B^{++}	C^{+++}	Be	B^+	C^{++}
PHP[a]	−0.0146	−0.0138	−0.0134	−0.0136	−0.0170	−0.0161	−0.0159
CI[b]	−0.0444	−0.0465	−0.0471	−0.0477	−0.0879	−0.1037	−0.1177
Exact[c]	−0.0453	−0.0475	−0.0489	−0.0498	−0.0944	−0.1123	−0.1268

[a] This work.
[b] A. W. Weiss, Phys. Rev. **122**, 1826 (1961). This calculation includes angular correlation.
[c] E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

The terms of Eq. (12) can be given the following interpretations: The first term is essentially the SCF wavefunction, the second is a doubly excited configuration, and the third and fourth are singly excited functions. We define Γ so that $z \equiv y/\Gamma$ is normalized, and using the property of $e^{(2,1)}$ pointed out above, Eq. (12) may be rewritten as

$$\begin{aligned}\Phi &= (\gamma_1+\gamma_2)e^{(2,1)}\{a'(1)x(2)x(3)-\Gamma^2 a(1)z(2)z(3)\\ &\quad+\delta\Gamma[a'(1)x(2)z(3)-a'(1)z(2)x(3)]\\ &\quad-(\langle a\mid x\rangle/\langle x\mid x\rangle)\delta\Gamma x(1)z(2)x(3)\}\\ &=\Phi_1-\Gamma^2\Phi_2+\delta\Gamma(\Phi_3-\Phi_4)-(\langle a\mid x\rangle/\langle x\mid x\rangle)\delta\Gamma\Phi_s,\end{aligned} \tag{13}$$

where

$$\delta=(\gamma_1-\gamma_2)/(\gamma_1+\gamma_2)$$

and

$$a'=a-(\langle a\mid x\rangle/\langle x\mid x\rangle)x.$$

It is seen that

$$\langle\Phi_1\mid\Phi_3\rangle=\langle\Phi_1\mid\Phi_4\rangle=0,$$

and hence these functions satisfy the orthogonality requirements of Brillouin's theorem with respect to the SCF function Φ_1. If we set $\gamma_2=0$, $\delta=1$, and in order to have a sizable contribution of Φ_2 in Φ, the contributions of Φ_3 and Φ_4 must be even larger. The term Φ_2 is the one which decreases the electronic repulsion in the correlation within the $1s$ shell. If, however, Φ_1 is the correct SCF function, terms Φ_3 and Φ_4 satisfy

$$\langle\Phi_1\mid H\mid\Phi_3\rangle=\langle\Phi_1\mid H\mid\Phi_4\rangle=0, \tag{14}$$

and the presence of these functions can only raise the calculated energy. The only way Φ_3 and Φ_4 could help would be to have Eq. (14) not apply, which means that Φ_1 cannot be the SCF function. However, this possibility is also very unsatisfactory since the SCF energy is very good. Thus the restriction $\gamma_2=0$ requires Γ to be very small and hence Γ^2 even smaller, and such a function produces essentially no correlation. If γ_1 and γ_2 are allowed to have their optimum values δ is very small $\sim$0.01 and this fact eliminates any major contribution from the undesirable terms Φ_3 and Φ_4 while allowing Γ to be larger and the desirable Φ_2 to have a larger contribution.

The simplest type of DODS calculation of Li is that given by Nesbet and Watson,[11] usually called spin-polarized Hartree–Fock, using a single Slater determinant. Löwdin[3] has suggested that the reason the spin-polarized calculations provide very little correlation is the fact that a DODS, single determinant, n-particle function is not a pure spin state. However, a very similar analysis to that of Eq. (13) can be made for a spin-polarized determinant, and it is seen that it has the same defects with respect to Brillouin's theorem as Eq. (13) does for $\delta=1$. Goddard's function is exactly equivalent to the result of applying the spin projection operator $O_{\frac{1}{2}\frac{1}{2}}$ to Nesbet's function. Therefore, the comparison of the correlation energy for Li of Nesbet and Watson, 0.00002 a.u., with that of Goddard, 0.00009 a.u., shows that removeal of the quartet state cannot alone guarantee a sizable increase in the correlation energy. It is necessary for the function to possess the flexibility to have the single excitation terms of the type of Φ_3 and Φ_4 multiplied by small coefficients.

It is interesting to make a conjecture concerning the result of removing the single excitation terms from the spin-polarized determinant without projecting a single spin state. It may be shown that this can be accomplished by replacing the single Slater determinant by the sum of two. Thus, in general, if the spatial orbitals $u_1, u_2, \cdots, u_k$ are associated with α spin functions and the spatial orbitals $v_1, v_2, \cdots, v_l$, $(l \leq k)$ are associated with β spin functions we may write

$$\begin{aligned}\Psi = &\mid u_1\alpha\cdots u_k\alpha v_1\beta\cdots v_2\beta\mid\\ &+\mid u_1\beta\cdots u_l\beta u_{l+1}\alpha\cdots u_k\alpha v_1\alpha\cdots v_l\alpha\mid.\end{aligned} \tag{15}$$

The first term of Ψ is just the spin-polarized determinant while the second term has the α's and β's interchanged for the paired orbitals. This function has no single excitation. So far as the authors are aware, this type of function has not been investigated, in general, however, the special case for doublet Li is equivalent to the function of Pauncz *et al.* and to that of Eq. (13) with $\gamma_1=\gamma_2$. In this one case, removing the single excitation also removes the quartet component so that here one cannot distinguish between the two effects. In general, the function of Eq. (15) contains several different multiplicity components. Comparison of the results of Nesbet and Watson to Goddard and the present article suggests, however, that removal of the single excitations is at least as important as the removal of the extraneous spin components.

[11] R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960).

The primitive idempotent $e^{(2,2)}$ has a factor $[I-(12)][I-(34)]$ in it similar to the one in $e^{(2,1)}$. In addition, however, it has a factor $[I+(14)(23)]$ which automatically removes the single excitations in an expansion such as that of Eq. (13). Therefore, we get from Eq. (8)

$$\begin{aligned}\Phi&\equiv e^{(2,2)}\psi\\&=(\gamma_1+\gamma_2)e^{(2,2)}\{u(1)x(2)x(3)u(4)\\&\quad-\Gamma_1^2v(1)x(2)x(3)v(4)-\Gamma_2^2u(1)y(2)y(3)u(4)\\&\quad+\delta\Gamma_1\Gamma_2[v(1)y(2)x(3)u(4)+u(1)x(2)y(3)v(4)\\&\quad-u(1)y(2)x(3)v(4)-v(1)x(2)y(3)u(4)]+\cdots\}\\&=\Phi_1-\Gamma_1^2\Phi_2-\Gamma_2^2\Phi_3+\delta\Gamma_1\Gamma_2\Phi_4+\cdots,\end{aligned}\tag{16}$$

where

$$\delta=(\gamma_1-\gamma_2)/(\gamma_1+\gamma_2)$$

as before, and

$$\begin{aligned}u&=\tfrac{1}{2}(a+d),\\x&=\tfrac{1}{2}(b+c),\\v&=(a-d)/2\Gamma_1,\ \langle v\mid v\rangle=1,\\y&=(b-c)/2\Gamma_2,\ \langle y\mid y\rangle=1,\end{aligned}$$

and we have omitted terms which can be interpreted as triple and quadruple excitations. Again Φ_1 is close to the restricted SCF function, and Φ_2 and Φ_3 are the terms giving the intrashell correlations. The four individual terms in Φ_4 are each of a type giving intershell correlation. From Table IV it is seen that $\gamma_1\cong\gamma_2$ so that δ is small and intershell correlation in these four-electron atoms is much smaller than intrashell correlation. This is physically reasonable since the $1s$-like electrons move much more rapidly than the $2s$-like electrons, resulting in a tendency to average out interactions in their motions. If the restriction $\gamma_2=0$ is applied, Eq. (16) gives a situation wherein the intershell and intrashell correlations must be more or less of the same importance. Goddard has given this case, and although his method gives the correlation energy of Be as 0.0142 a.u., which is considerably greater than for Li, this is less than the value for Be^{++}, 0.0145 a.u. Table IV shows that when γ_1 and γ_2 have their optimum values, the correlation energy in Be is greater than that in Be^{++}.

The presence of a factor in $e^{(\mu)}$ which will annihilate the single excitation terms depends on the shape of tableaux, and such a factor occurs only for $[2^{n/2}]$ tableaux, that is, in the singlet case. If, however, $\theta'PNP$ were used for $e^{(\mu)}$, the single excitation terms would be annihilated for all cases (except $S=n/2$ where there is no pairing at all). In spite of this, the relative simplicity of θNPN makes us prefer to use this operator. Thus, the sum over the standard tableaux in Eq. (4) gives the wavefunction the flexibility to (a) contain very little single excitation type component and (b) at the same time allows inter- and intrashell correlations to take on differing importances.

The AMO procedure for alternant systems suggested by Löwdin[3] (see also Ref. 12) is an approximate form of the projected Hartree–Fock procedure. In II it was shown that the projection of a single DODS determinant for the principle case ($M_S=S$) is equivalent to the present treatment for

$$\gamma_2=\gamma_3=\cdots=\gamma_f=0.$$

The π system of the benzene molecule has been treated quite successfully with the AMO technique, but in benzene the electrons in the various shells have a much smaller spread in velocities than in Be, therefore, the single tableaux with more or less equal inter- and intrashell correlations is much more appropriate. The standard AMO prescription calls for the projection not of the principle case but of the DODS determinant for $M_S=0$. Except for singlet cases this yields a result different from our $e^{(\mu)}$. In fact, such a procedure annihilates all single excitations for all odd multiplicity systems, and hence is expected to be considerably more successful than the projection of the principle determinant.[12]

We have collected together in Table V the values of the correlation energies obtained in this study along with values from a more general treatment and the "exact" values. In the three-electron systems it is seen that radial correlation accounts for approximately one third of the total, and in the four-electron systems approximately one fifth of the total. Work is underway to include angular correlation into this treatment by the use of spatial projections.

ACKNOWLEDGMENTS

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[12] R. Pauncz, *Alternant Molecular Orbital Method* (W. B. Saunders Co., Philadelphia, Pa., 1967).